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Supporting Information

A new tetrazolate zeolite-like framework for highly selective CO_2/CH_4 and CO_2/N_2 separation

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Materials and Methods:

All reagents and solvents were used as received from commercial suppliers without further purification. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 3 K $\min^{-1}$ from 30 to 800 ℃. Powder X-ray diffraction (PXRD) patterns were recorded by a RigakuUltima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 deg $\min^{-1}$.

Preparation of UTSA-49:

A mixture of Hmtz-5 (5.00mg, 0.0079mmol) and $Zn(NO_3)_2$•$6H_2O$ (30.00mg, 0.0587mmol) was dissolved in DMF/EtOH (2.5mL, 4:1, v/v) in a screw-capped vial (20 ml). The vial was capped and placed in an oven at 90℃ for 24 h. The resulting colourless block single crystals were washed with DMF several times to give **UTSA-49**. Elemental analysis: Calcd. for $[Zn(mtz\text{-}5)_2]$• (DMF)•H_2O ($C_7H_{15}N_9O_2Zn_2$): C, 26.06%; H, 4.69%; N, 39.07%; Found: C, 26.32%; H, 4.77%; N: 38.83%.

Gas Adsorption Measurements

A QUDRASORB SI-M surface area analyzer was used to measure gas adsorption isotherms. To have a guest-free framework, the fresh sample was guest-exchange with dry methanol 3 times per day for 3 days, filtered and vacuumed at 23 ℃ for 10 hours to measurements. A sample of 111.0 mg was used for the sorption measurements and was maintained at 77 K with liquid nitrogen and at 273 K with an ice−water bath. As the center-controlled air conditioner was set up at 23 ℃, a water bath was used for adsorption isotherms at 298 K.

Single-Crystal X-ray Structure Determination. Single crystal X-ray diffraction was performed with an Oxford Diffraction Gemini S Ultra CCD diffractometer equipped with graphite-monochromated Mo−Kα (λ =0.71073 Å) using "multiscan" technique at 293K. The structure was solved by WinGX and refined by a matrix least-squares method using SHELXL-97 programs. The non-hydrogen atoms were refined anisotropically. Disordered, independent solvent molecules inside the frameworks were eliminated in the refinement by PLATON/SQUEEZE.

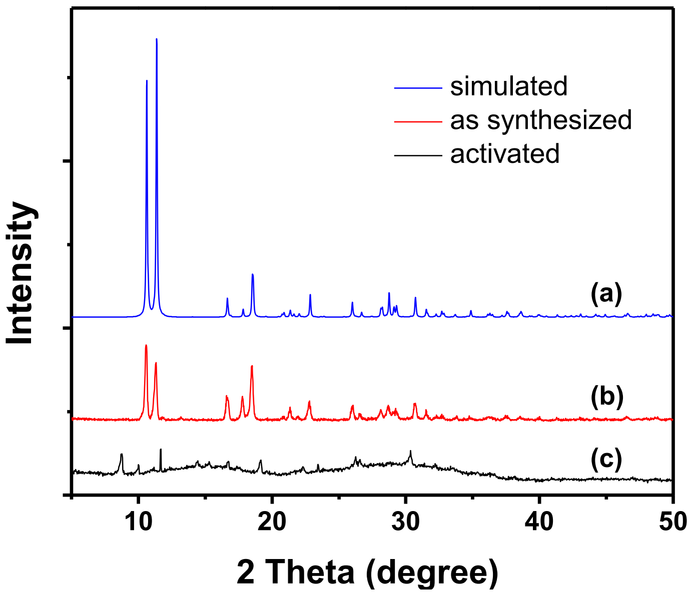

Figure S1. PXRD patterns of as-synthesized **UTSA-49** (b) and activated **UTSA-49a** (c) along with the simulated pattern from its single crystal X-ray structure (a).

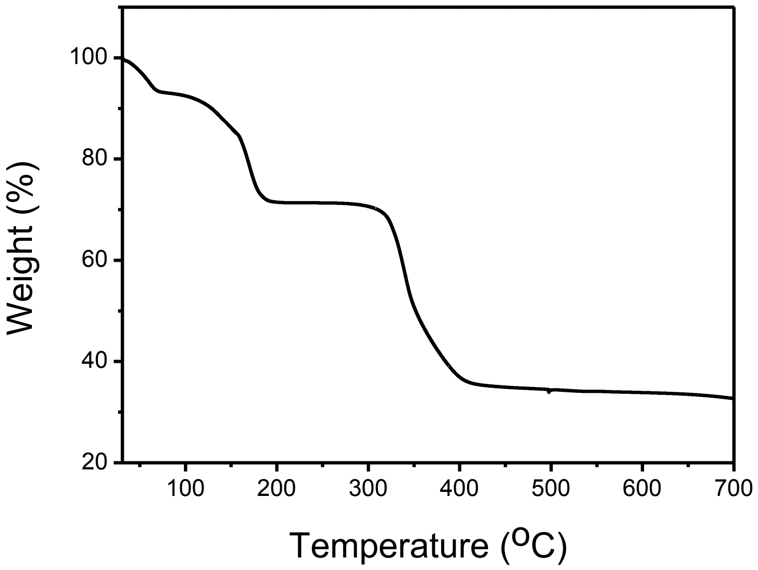

Figure S2. TGA curves of as-synthesized **UTSA-49**

Table S1. Crystal data and structure refinement for **UTSA-49**

	UTSA-49
chemical formula	$C_{16}H_{24}N_{32}$Zn4
formula weight	926.15
temperature (K)	293(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	Pc
a (Å)	19.2148(14)
b (Å)	13.3436(8)
c (Å)	10.6713(5)
α (°)	90.00
β (°)	95.038(6)
γ (°)	90.00
V (Å^3)	2725.5(3)
Z	2
density (calculated g/cm^{-3})	1.129
absorbance coefficient (mm^{-1})	1.781
F(000)	928
crystal size (mm^3)	0.36×0.33×0.32
goodness of fit on F_2	1.007
R_{int}	0.0407
R1, wR2 (I>2σ(I)^a	0.0486, 0.1270
R1, wR2 (all data)^a	0.0780, 0.1374

^{a}R1 = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; wR2 = $|\Sigma w(|F_o|-|F_c|^2) / \Sigma w F_o{}^2]^{1/2}$

Table S2. Selected bond length (Å) for UTSA-49

Bond	Bond length (Å)	Bond	Bond length (Å)
Zn1-N20	1.990(6)	Zn3-N8	2.048(9)
Zn1-N11	2.018(7)	Zn3-N35	1.975(7)
Zn1-N19	1.987(6)	Zn3-N34	2.008(7)
Zn1-N7	1.962(8)	Zn3-N3	2.012(8)
Zn2-N25	1.947(7)	Zn4-N4	2.014(7)
Zn2-N26	1.974(7)	Zn4-N27	1.995(7)
Zn2-N14	2.018(8)	Zn4-N16	2.004(8)
Zn2-N12	1.992(8)	Zn4-N30	1.975(7)

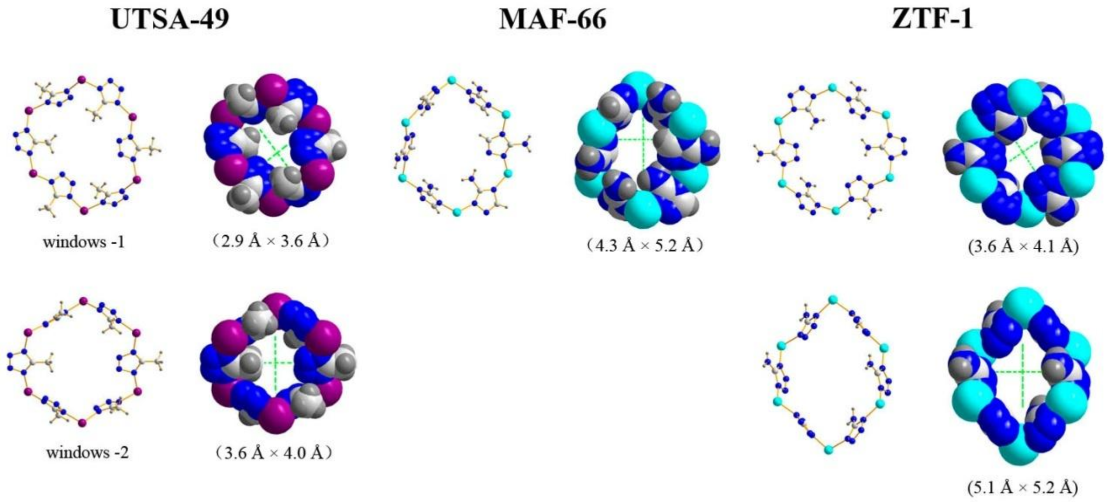

Figure S3. The 6-membered ring windows diagram and the pore aperture contrast for UTSA-49, MAF-66 and ZTF-1. The pore sizes were calculated using the Diamond 3.0d software (considering the Van der Waals radii of constituting atoms).

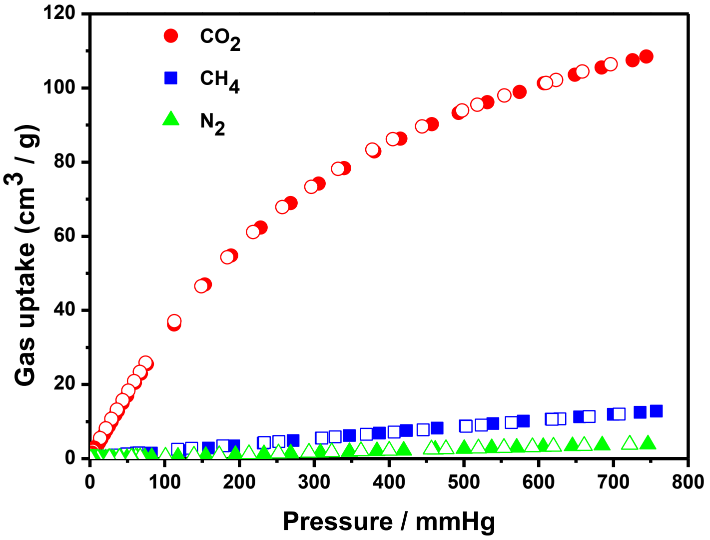

Figure S4. Adsorption (solid) and desorption (open) isotherms of carbon dioxide ((red circles), methane (blue squares), and nitrogen (green triangles) on UTSA-49a at 273 K.

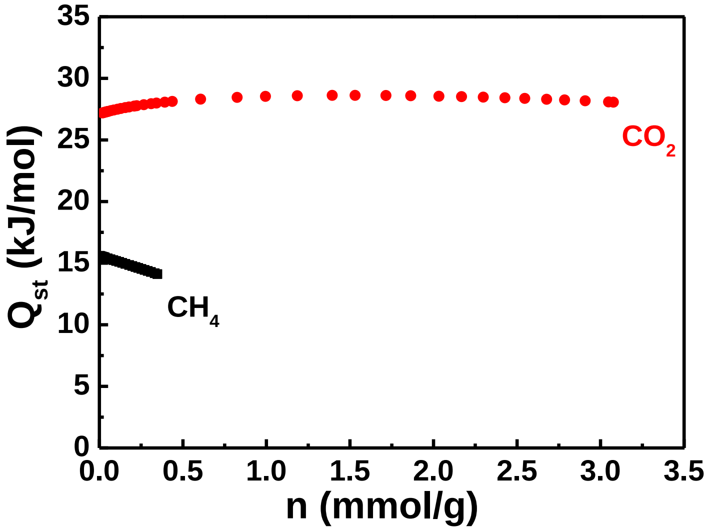

Figure S5. The variation of Q_{st} with amount adsorbed for CO_2 (red circles) and CH_4 (black squares).

Table S3. CO_2 uptakes and separation in selected MOFs.

Sample	CO_2/CH_4 selectivity	CO_2/N_2 selectivity	CO_2 uptake (wt%)	Temperature (k)	Ref
ZIF-68	5	18.7	7.39	298	1
ZIF-69	5.1	19.9	7.98	298	1
ZIF-70	5.2	17.3	10.8	298	1
ZIF-78	10.6	50.1	10.1	298	1
ZIF-79	5.4	23.2	6.58	298	1
ZIF-81	5.7	23.8	7.50	298	1
ZIF-82	9.6	35.3	10.4	298	1
ZIF-95	4.3 ± 0.4	18 ± 1.7	3.87	298	1
ZIF-100	5.9 ± 0.4	25 ± 2.4	6.40	298	1
MAF-66	5.8^{a}	225^{a}	19.4	298	2
	7.5^{a}	403^{a}	27.6	273	
ZTF-1	NA	NA	16.6	298	3
	NA	NA	23.5	273	
UTSA-49	33.7^{b}	95.8^{b}	13.6	298	This work
	34.8^{b}	197.7^{b}	21.3	273	
IFMC-1	NA	26.9	11.8	298	4
	NA	50.3	18.0	273	
[Zn(btz)]	15.3^{a}	NA	22.4	298	5
	21.1^{a}	NA	35.6	273	
Mg_2(dobdc)	137^{b}	NA	35.2	298	6
MAF-25	NA	NA	5.3	273	7
MAF-26	NA	NA	4.1	273	7
MAF-7	NA	NA	5.3	298	8
MAF-4	NA	NA	3.1	298	8
MAF-2	NA	NA	3.6	298	9

^{a}Henry's law selectivity. ^{b}IAST selectivity.

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Ideal Adsorbed Solution Theory:

The ideal adsorbed solution theory (IAST)[10] was used to predict the equimolar binary mixture adsorption of CO_2 and CH_4 from the experiment pure-gas isotherm. The single-component isotherms were fit to a dual-site Langmuir-Freundlich equation:

$$q = q_{m1} \bullet \frac{b_1 \bullet P^{1/n_1}}{1 + b_1 \bullet P^{1/n_1}} + q_{m2} \bullet \frac{b_2 \bullet P^{1/n_2}}{1 + b_2 \bullet P^{1/n_2}} \qquad (1)$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol/kg). b_1 and b_2 are affinity coefficient of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. Although this is not the only model that can be used to fit the data, IAST requires a precise fit of the experimental data to the model in order to accurately perform the necessary integrations.[11-13]

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Dual Site Langmuir-Freundlich Model for CO_2/CH_4, and CO_2/N_2 Adsorption Isotherms

On the basis of the Dual site Langmuir-Freundlich (DSLF) model: (**II**)

$$N = N_1^{\max} \times \frac{b_1 p^{1/n1}}{1+b_1 p^{1/n1}} + N_2^{\max} \times \frac{b_2 p^{1/n2}}{1+b_2 p^{1/n2}} \quad \textbf{(II)}$$

Where p (unit: Kpa) is the pressure of the bulk gas at equilibrium with the adsorbed phase, N (unit: mol/Kg) is the adsorbed amount per mass of adsorbent, N_1^{max} and N_2^{max} (unit: mol/Kg) are the saturation capacities of sites 1 and 2, b_1 and b_2 (unit: 1/kPa) are the affinity coefficients of sites 1 and 2, and n_1 and n_2 represent the deviations from an ideal homogeneous surface. Here, the single-component CO_2, CH_4, and N_2 adsorption isotherms have been fit to enable the application of IAST in simulating the performance of UTSA-49a under a mixed component gas. The fitting parameters of DSLF equation are listed in Table S5. Adsorption isotherms and gas selectivities calculated by IAST for mixed CO_2/CH_4 (CO_2/CH_4 = 50:50), CO_2/N_2 (CO_2/N_2 = 10:90, 15:85, and 20:80) in the UTSA-49a.

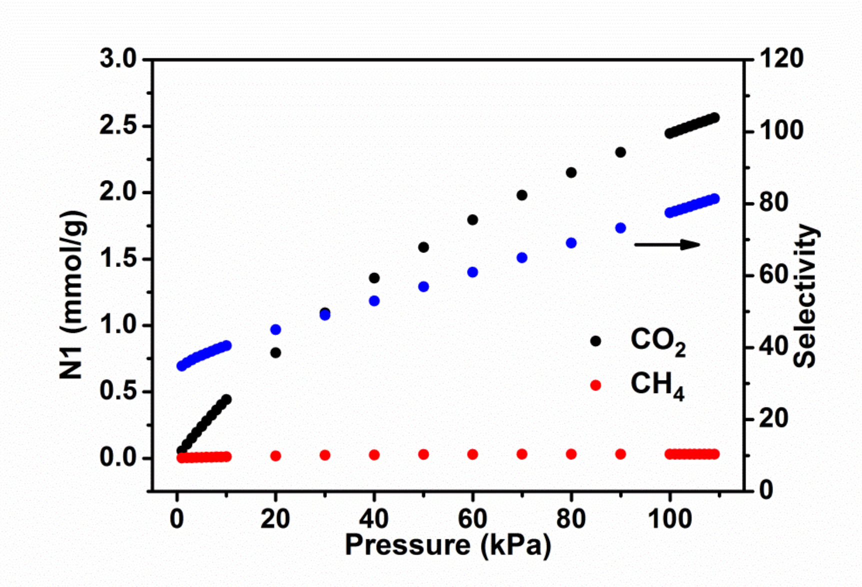

Figure S6. Mixture adsorption isotherms and adsorption selectivity predicted by IAST of UTSA-49a for CO_2 (50%) and CH_4 (50%) at 273 K.

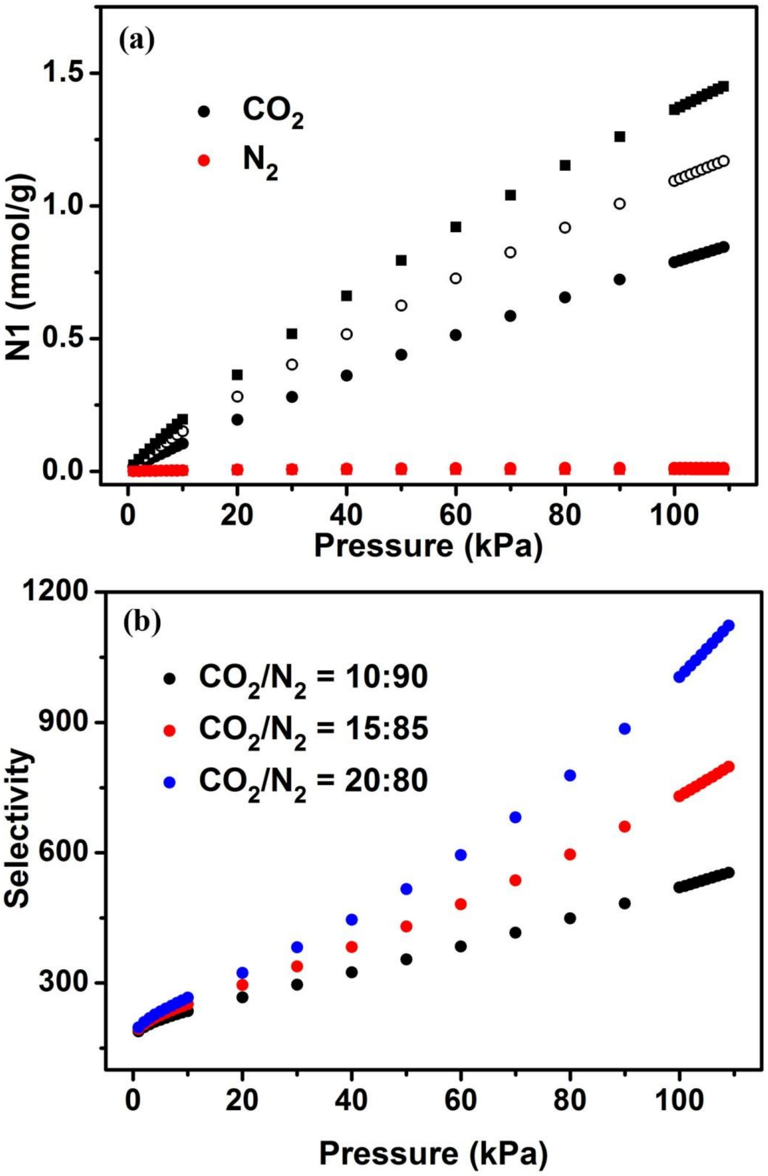

Figure S7. Mixture adsorption isotherms (a) and adsorption selectivity (b) predicted by IAST of UTSA-49a for CO_2 and N_2 (10:90, 15:85, and 20:80) at 273 K.

Table S4. IAST selectivities of CO_2/CH_4 (CO_2/CH_4 = 50:50) and CO_2/N_2 (CO_2/N_2 = 10:90, 15:85, 20:80).

mixture	Temperature (K)	component proportion	IAST selectivity
CO_2/CH_4	273	50:50	34.8
CO_2/N_2	273	10:90	188.8
CO_2/N_2	273	15:85	193.7
CO_2/N_2	273	20:80	197.7
CO_2/CH_4	298	50:50	33.7
CO_2/N_2	298	10:90	90.5
CO_2/N_2	298	15:85	93.5
CO_2/N_2	298	20:80	95.8

Table S5. Equation parameters for the DSLF isotherm model.

Adsorbates	N_1^{max} (mmol/g)	b_1 (kPa-1)	n_1	N_2^{max} (mmol/g)	b_2 (kPa-1)	n_2
CO_2 (273 K)	3.5525	0.01784	1.0041	3.2596	0.01324	0.8131
CH_4 (273 K)	1.0911	0.00216	0.8970	0.9980	0.00200	0.8834
N_2 (273 K)	0.6561	0.00152	0.8524	0.1501	0.00013	0.7831
CO_2 (298 K)	4.0375	0.00508	0.9684	3.7415	0.00434	0.9051
CH_4 (298 K)	0.7278	0.00124	0.8606	0.8230	0.00090	0.7830
N_2 (298K)	0.2496	0.00189	0.8986	0.1793	0.00064	0.7043